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(54) ELECTROCHEMICAL CELL

(57)Abstract:

PURPOSE: To improve conductivity and reliability at a small Ni inclusion ratio by approximating thermal expansion coefficients between those of a hydrogen electrode and a solid electrolyte while adopting a substance, wherein  $\text{La}_{x-1}\text{Sr}_x\text{Cr}_z\text{O}$  ( $x-z=\text{a specific value}$ ) is mixed into NiO at respective specific wt. ratio, as the hydrogen electrode.

CONSTITUTION: A substance, wherein La Sr CO ( $x=0.05-0.02$ ) is mixed into NiO at a ratio of 30-60% to 70-40 % in a wt. ratio, is adopted as a hydrogen electrode. For instance, an LSC particle 4 and NiO use a substance having a mol ratio of La<sub>0.2</sub> Sr<sub>0.8</sub> CrO<sub>3</sub> and a particle diameter of 2 $\mu$ m and a substance having a particle diameter of 2 $\mu$ m, respectively, and are mixed so as to have a wt. ratio of NiO:LSC=60:40. In a fuel electrode 2, wherein a resultant mixture is adopted as slurry to be applied onto a solid electrolyte (YSZ) 1 to be baked at 1400°C, the reaction of  $H_2+O_2 \rightarrow H_2O+2e$  is caused and a conductivity inspection can be possible. Also, a 3-phase interface can be enlarged because a thermal expansion coefficient approximates the electrolyte 1, conductivity as high as about 700 S/cm can be obtained by a small Ni content, and all electrode surfaces have conductivity. Consequently, conductivity and reliability can be improved.

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## DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Industrial Application]

This invention relates especially to the hydrogen electrode about a solid oxide type electrochemistry cell [ as / in an elevated-temperature solid oxide fuel cell or a high-temperature-steam solid oxide type electrolytic device ].

[0002]

[Description of the Prior Art]

Since an elevated-temperature solid oxide fuel cell and a high-temperature-steam solid oxide type electrolytic device are only reverse reaction electrochemically, the former is hereafter taken and explained to an example. Although it is made to generate electricity by an elevated-temperature solid oxide fuel cell supplying fuels, such as hydrogen, and oxidizers, such as air, to electrolytic both sides, the configuration is as being shown in drawing 3 . In the configuration of drawing 3 , nickel-YSZ (yttria stabilized zirconia) was used and the quantitative percentage of the fuel electrode 2 was 60 - 70% : 40 - 30% as a weight ratio of NiO:YSZ. in addition, drawing 3 -- setting -- 1 -- a solid electrolyte (the quality of the material is YSZ) and 3 -- in nickel particle and 5, a steam (H<sub>2</sub> O) and 8 show an electron and, as for a YSZ particle and 6, 9 shows oxygen ion, as for hydrogen (H<sub>2</sub>) and 7.

[0003]

[Problem(s) to be Solved by the Invention]

The trouble in the case of the conventional elevated-temperature solid oxide fuel cell is described below. As shown in drawing 3 , the mixture (called a cermet) of NiO and YSZ is conventionally common as a fuel electrode of a solid oxide fuel cell. Although NiO serves as Metal nickel under a service condition and the excellent electrode engine performance is demonstrated, since it is a metal, it is common for coefficient of thermal expansion not to be in agreement with a solid electrolyte like YSZ, and to mix YSZ at the sacrifice of conductivity for the adjustment, and it has prevented that do in this way and a fuel electrode exfoliates from a solid electrolyte.

[0004] In the case of this conventional fuel electrode (a nickel-YSZ electrode is called), there were the following faults.

(1) In order to use NiO at the time of manufacture, it is necessary to perform reduction actuation before use. Since it is an insulator until it carries out reduction actuation, there is no conductivity.

(2) Since YSZ is an electronic insulator, if it is going to raise the conductivity of a nickel-YSZ system electrode for the improvement in the engine performance of a

fuel cell, it is necessary to make the content of NiO increase, and this becomes the cause which coefficient of thermal expansion leaves further with a solid electrolyte.

[0005] This invention tends to offer the electrochemistry cel from which such a problem is eliminated, there is conductivity also before use and high conductivity is obtained also in comparatively little NiO content.

[0006]

[Means for Solving the Problem]

This invention is an electrochemistry cel characterized by becoming considering what mixed  $\text{La}_{1-x}\text{Sr}_x\text{CrO}_3$  ( $x=0.05-0.20$ ) 30 - 60% : 70 to 40% by the weight ratio to NiO as a hydrogen electrode.

[0007] That is, the following means are taken in this invention.

(1) here [ the point and here ] which replaced with the mixed stock of conventional NiO-YSZ as a hydrogen electrode of an electrochemistry cel here, and were made into the nickel-LSC system -- LSC --  $\text{La}_{1-x}\text{Sr}_x\text{CrO}_3$  from -- it is the becoming perovskite mold oxide and is the range of  $x=0.05-0.20$ .

(2) The point which replaced the appending rate of NiO with to 60 - 70 conventional%, and was decreased to 30 - 60%.

[0008]

[Function]

An operation of this invention is taken and explained to the example of an elevated-temperature solid oxide fuel cell. The next reaction starts in the fuel electrode of an elevated-temperature solid oxide fuel cell.



Namely, the hydrogen supplied to the electrode reacts with the oxygen ion which came from the solid electrolyte, generates water, and generates electricity by emitting an electron. Although it is necessary to take out this electron outside in order to maintain a generation of electrical energy, for that, an electrode needs to be a good electronic conductor. Since nickel bears electronic electric conduction as usual in the electrode of this invention and also LSC has electronic conductivity in oxidation reduction both ambient atmospheres, the former and equivalent electron conductivity can be demonstrated with nickel content smaller than before.

[0009] Moreover, although the reaction shown by above (1) occurs only by the so-called three-phase-circuit interface of an electrode, a solid electrolyte, and a gas phase, since all the front faces of an electrode have electronic conductivity

according to this invention, a three-phase-circuit interface can be enlarged.

Furthermore, since LSC is used in the case of this invention, in such a case, flow inspection is possible [ since there is no electronic conductivity in the case of the conventional NiO-YSZ system electrode material before performing reduction actuation before use (NiO is an insulator), flow inspection is impossible, but ].

[0010] Since a fuel electrode is formed on a solid electrolyte (usually YSZ), if coefficient of thermal expansion differs not much, it may exfoliate.  $\text{La}_{1-x}\text{Sr}_x\text{CrO}_3$  is in agreement with the coefficient of thermal expansion of YSZ by about 0.16. Or more by  $x=0.2$ , since coefficient of thermal expansion exceeds YSZ, it cannot be used. When smaller than  $x=0.16$ , coefficient of thermal expansion will be smaller than YSZ, but since NiO with a large coefficient of thermal expansion is mixed, there is especially no problem. On the other hand, when it is made smaller than  $x=0.05$ , it is  $\text{La}_{1-x}\text{Sr}_x\text{CrO}_3$ . Since \*\*\*\*\* becomes that conductivity does not have less, electrode performance degradation is brought about.  $\text{La}_{1-x}\text{Sr}_x\text{CrO}_3$  used by this invention from these things  $x$  becomes a value with desirable 0.05-0.20.

[0011] Moreover, when NiO is smaller than 30%, it is  $\text{NiO-La}_{1-x}\text{Sr}_x\text{CrO}_3$ . The conductivity of a mixed electrode serves as 1 S/cm (inside of hydrogen) extent,



and the electrode engine performance worsens. This is because the particle comrade of nickel exists independently, so conductivity will fall. When NiO becomes larger than 60%, it is  $\text{NiO-La}_{1-x}\text{Sr}_x\text{CrO}_3$ . The coefficient of thermal expansion of a mixed electrode becomes larger than  $12 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$ , and it exfoliates almost certainly from a solid electrolyte (YSZ: coefficient-of-thermal-expansion  $10 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$ ). Although the mixing ratio of NiO used by this invention is made 30 - 60% from such a viewpoint, the desirable range is 40 - 55%.

[0012]

[Example]

By drawing 1 , one example by this invention is taken for an example, and an elevated-temperature solid oxide fuel cell is explained. Drawing 1 shows the enlarged drawing of a fuel electrode, and, in the case of this example, manufactured it by the following specification. In drawing 1 , since the same sign as drawing 3 shows the same thing as drawing 3 , explanation is omitted. It is only differing from drawing 3 in that 4 is LSC. NiO uses a thing with a particle size of 1 micrometer, and LSC is  $\text{La}_{0.20}\text{Sr}_{0.80}\text{CrO}_3$ . The weight ratio was mixed in  $\text{NiO:LSC}=60:40$  using the thing with a particle size [ of a mole ratio ] of

2 micrometers. It applied on the solid electrolyte (YSZ) by having made this into the slurry, and calcinated at 1400 degrees C.

[0013] The data of the conductivity in 1000 degrees C under the hydrogen ambient atmosphere of used NiO-LSC and an air ambient atmosphere are shown in drawing 2 . In drawing 2 , a continuous line shows the case where LSC is used and a dotted line shows the case where YSZ is used. From drawing 2 , the high conductivity of about 700 S/cm was obtained in hydrogen, and the hydrogen electrode of this example had the conductivity of several S/cm also in the air before performing reduction actuation.

[0014]

[Effect of the Invention]

The following effectiveness is born by this invention.

(1) Since nickel bears electronic electric conduction as usual in the electrode of this invention and also LSC has electronic conductivity in oxidation reduction both ambient atmospheres, the former and equivalent electron conductivity can be demonstrated with nickel content smaller than before. For example, in the case of this invention, in 60% of NiO content, the high conductivity of about 700 S/cm is obtained to the conductivity in the case of a conventional method being

only about 30 S/cm. That it is little nickel content means that coefficient of thermal expansion is more as near as a solid electrolyte (YSZ).

(2) In the case of a conventional method, electrode reaction occurs only by the so-called three-phase-circuit interface of an electrode, a solid electrolyte, and a gas phase, but since all the front faces of an electrode have electronic conductivity according to this invention, a three-phase-circuit interface can be enlarged. This leads to the improvement in the engine performance.

(3) Although flow inspection is impossible since there is no electronic conductivity in the case of the conventional NiO-YSZ system electrode material before performing reduction actuation before use (NiO is an insulator), in the case of this invention, the conductivity of several S/cm is in air. This is because LSC which has conductivity under both the ambient atmospheres of oxidation reduction is used, and, in such a case, flow inspection is possible for it. This leads to improvement in dependability.

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## TECHNICAL FIELD

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[Industrial Application] This invention relates especially to the hydrogen electrode about a solid oxide type electrochemistry cel [ as / in an

elevated-temperature solid oxide fuel cell or a high-temperature-steam solid oxide type electrolytic device ].

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

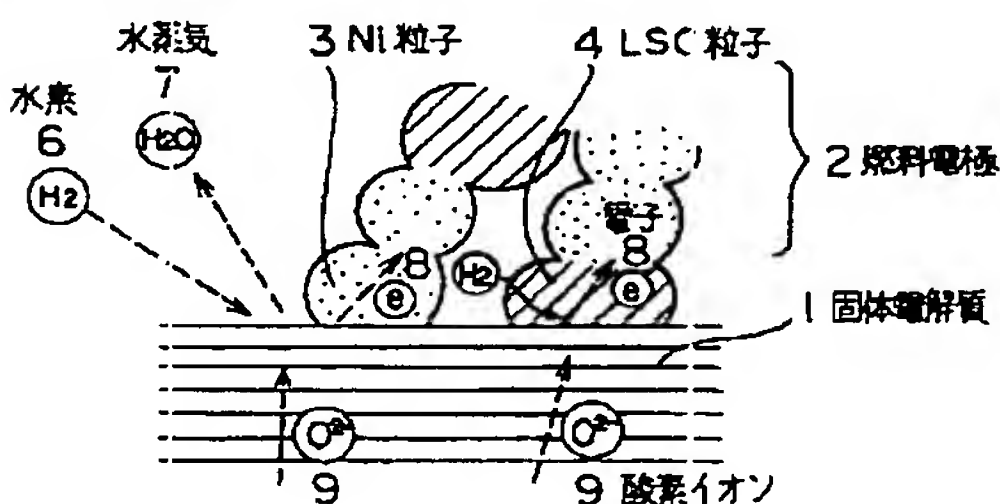
[Drawing 1] Drawing having shown the concept of the fuel electrode of the fuel cell concerning one example of this invention.

[Drawing 2] Drawing having shown the conductivity of nickel-LSC of this invention.

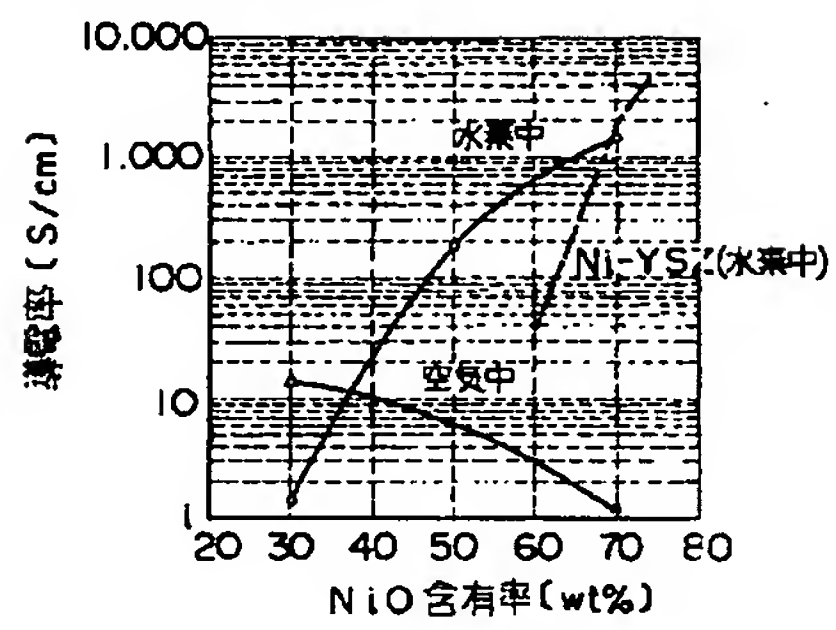
[Drawing 3] Drawing having shown the concept of the fuel electrode of the conventional fuel cell.

DRAWINGS

[Drawing 1]



[Drawing 2]



[Drawing 3]

